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FACTORS IN THE STABILITY OF VEGETABLE-CHROME COMBINATION-TANNED LEATHERS

II. THE EXTRACTION OF CHROMIUM FROM CHROME LEATHER BY VEGETABLE TANNING EXTRACTS*

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ABSTRACT

Evidence for the interaction of vegetable tans with chromium was presented in the preceding paper, and its significance in connection with the deterioration of semichrome and chrome retan leathers was discussed.

The present paper deals with the losses in chromium and falls in shrinkage temperature resulting from the prolonged treatment of chrome leather in solutions of vegetable tanning extracts.

The three vegetable tanning materials examined (myrobalans, mimosa, and sulfited quebracho), tannic acid, catechol, and pyrogallol all extracted appreciable amounts of chromium and caused falls in shrinkage temperature of up to 25°C. Most of this detannage occurred in the first few days but continued slowly over periods up to 30 days at 40°C. Both losses in chromium and falls in shrinkage temperature increased with the temperature of extraction and with fall in pH.

Pyrogallol and catechol were very effective both with respect to extraction of chromium and reduction in shrinkage temperature. On a comparable tan basis the extraction of chromium increased in the order : myrobalans < tannic acid < mimosa < quebracho and the falls in shrinkage temperature in the order : quebracho < mimosa < myrobalans < tannic acid. Extraction of chromium is complicated by precipitation of vegetable tan–chromium complexes, and the fall in shrinkage temperature is a more reliable guide to the extent of detannage. It is, therefore, concluded that from the standpoint of deterioration quebracho is the most suitable tanning material to use in conjunction with chromium.

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INTRODUCTION

In the previous paper (1) evidence was presented for the interaction of chromium with tannic acid and the constituents of vegetable tanning extracts. Little information regarding the quantitative aspects of the interaction was obtained, however, and no definite statement concerning the extent to which different tanning materials were likely to displace protein carboxyl groups from the chromium complex was possible.

An attempt has now been made to obtain more direct evidence on this point from a study of the extraction of chromium and fall in shrinkage temperature resulting from the treatment of chrome leather in solutions of tanning materials for long periods of time. Feher and Kerese (2) have also approached the problem from this angle but limited their determinations to loss of chromium from the leather and to tanning materials used in Hungary. These did not include mimosa and myrobalans, which are commonly used in Great Britain. Extractions were made either at the natural pH of the tanning extract or after adjustment to pH 3.5 with formic acid or sodium carbonate. The choice of this acid for the adjustment of pH will obviously have had an influence on the amounts of chromium extracted.

EXPERIMENTAL

Materials.—A wet chrome-tanned hide side was obtained from the tannery and acetone-dehydrated. This had been processed commercially and chrome-tanned in a basic chromic sulfate liquor. The chromic oxide content was 5.11% on air-dry weight, and the shrinkage temperature was 105 °C. The leather was cut into pieces 1 x 5 cm., all with their longer dimension perpendicular to the backbone, and these pieces were thoroughly mixed. Concentrated solutions of vegetable tan were made up from commercial liquid extracts of mimosa and lightly sulfited quebracho and from solid myrobalans. Solutions of tannic acid, pyrogallol, catechol, and resorcinol were made up using laboratory reagent chemicals. The solutions were diluted, and their pH was adjusted as required with hydrochloric acid or sodium hydroxide. Total solids, tans, and nontans of the extracts of the concentrated solutions are given in Table I.

TABLE I

ANALYSIS OF CONCENTRATED TANNING SOLUTIONS

(*g. per* 100 *g. solution*)

	Total Solids	Tans	Nontans
Tannic acid	15.1	13.9	1.2
Myrobalans	27.3	18.6	8.7
Mimosa	27.3	18.9	8.4
Sulfited quebracho	34.8	28.9	5.9

Extractions.—Six grams leather were treated with 200 ml. of tanning solution in stoppered bottles under the conditions specified. After the appropriate periods of time the pieces were rinsed in water and air-dried. The shrinkage temperature of the leathers and the pH and the chromium content of the extracts were determined. The total chromium extracted was calculated, and results were expressed as chromium retained by the leather as a percentage of that originally present.

Methods of analysis.

Tans and nontans in the vegetable tanning solutions were determined by the Official Method of S.L.T.C. (3).

Chromium in the leather and solutions was determined by perchloric acid oxidation followed by titration with ferrous ammonium sulfate (4). With the solutions it was necessary to add several times the normal amount of nitric acid in the early stages of the determination in order to oxidize the vegetable tan and phenolic compounds.

pH of water extract. The leather was cut into pieces about 0.5 cm. square, and 2.5 g. was immersed in 50 ml. water for 48 hours.

Shrinkage temperature. The samples were wet back in water under reduced pressure and then heated in liquid paraffin. This medium was used in preference to a 75% v/v glycerol-water mixture, as the latter tends to give low values for leathers containing vegetable tan (5). In some experiments determinations were also made in water, using an apparatus designed for measurements under pressure (6). There was virtually no difference between the two methods of determination, and with both replicate determinations varied by 2°–3°C.

RESULTS

Three series of experiments were carried out in each of which samples of the chrome leather were extracted for varying periods of time with solutions of vegetable tanning extracts or phenolic compounds.

(1) Extraction with solutions of mimosa, sulfited quebracho, and myrobalans containing 13.4% w/v tan, i.e., 80 g. tan per g. Cr_2O_3 in the leather, at 20° and 40°C.

(2) Extraction with 13.4% w/v tan solutions of sulfited quebracho at 40°C. and various pH values.

(3) Extraction with 6.7% w/v tan solutions of myrobalans, mimosa, sulfited quebracho, and tannic acid and 3% solutions of catechol, pyrogallol, and resorcinol at 40°C.

Results are presented graphically in Figs. 1 to 6 in which the percentage chromium retained by the leather (expressed as g. Cr_2O_3 per 100 g. original

air-dry leather) and the shrinkage temperature are plotted against time. Each point is the mean of two duplicate extractions.

During the extractions the leather samples treated with the vegetable tanning solutions became progressively darker in color and in many cases were very brittle and cracky. Samples treated in catechol and pyrogallol were almost black in color but were not cracky, while those treated in resorcinol were not obviously changed.

In all cases the pH fell sharply during the first day of extraction, and subsequently there were only minor fluctuations (Table II). The fall is presumably due to displacement of sulfate ions from the chromium complex either by reason of olation or replacement by weak organic acid anions and by the hydroxy groups of the phenolic compounds. This fall was also observed with resorcinol, which shows little tendency to complex with chromium (1, 7). Subsequently the leather was found to be rather acid (the pH of water extract was 2.6),and this may have been a contributory cause.

TABLE II

pH VALUES OF SOLUTIONS DURING EXTRACTIONS

Time	Myrobalans		Mimosa		S. Quebracho	
	20° C.	40° C.	20° C.	40° C.	20° C.	40° C.
Experiment I						
0 days	3.5	3.5	3.5	3.5	3.5	3.5
1 day	3.1	3.0	2.9	2.9	3.5	3.4
20 days	3.2	3.0	2.9	2.8	3.2	3.2

Experiment II		*Quebracho at 40° C.*			
0 days	2.5	3.0	3.5	4.0	4.5
4 days	2.4	2.6	2.9	3.3	3.6
34 days	2.3	2.6	2.9	3.2	3.5

Experiment III	*Extraction at 40° C.*						
	Myro-balans	Mimosa	S. Que-bracho	Tannic Acid	Catechol	Pyro-gallol	Resor-cinol
0 days	4.0	4.0	4.0	4.0	4.0	4.0	4.0
1 day	3.0	2.9	2.8	2.1	2.4	2.2	2.6
32 days	3.0	2.8	2.8	2.1	2.3	2.1	2.7

In the first experiment, in which the effects of extraction with solutions of myrobalans. mimosa, and sulfited quebracho at 20° and 40°C. were com-

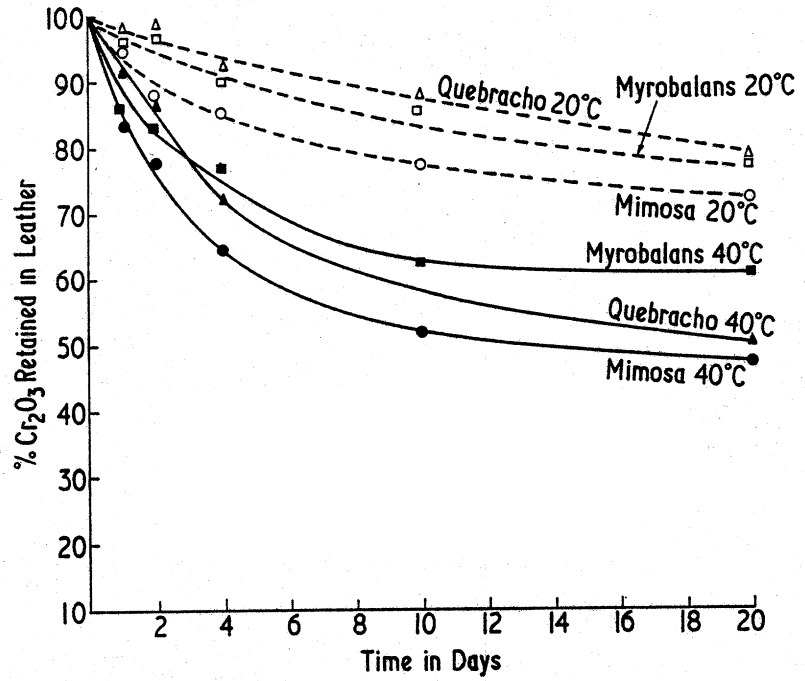

FIGURE 1.—Percentage chromium retained in chrome leather after treatment in tan solutions at 20°C. (broken lines) and 40°C. (continuous lines).

	20°C.	40°C.
Myrobalans	□	■
Mimosa	○	●
Sulfited Quebracho	△	▲

pared (Figs. 1 and 2), the initial pH was 3.5. Even at 20°C. between 20% and 30% of the chromium was extracted in 20 days, and there was little indication that an equilibrium was being approached. At 40°C. the amounts extracted were approximately doubled, about 50% being extracted by mimosa and quebracho and 40% by myrobalans. The falls in shrinkage temperature did not necessarily run parallel with the drop in chromium content. With quebracho at 20°C. there was no decrease in shrinkage temperature over periods of up to 20 days, but with mimosa and myrobalans there was a sharp decrease in the first few days followed by a slower decrease. At 40°C. there were marked decreases with all three materials, particularly with myrobalans. With this tanning material the shrinkage temperature was reduced to 83°C. in 4 days, but there was little further decrease during the following 16 days. Presumably the limiting value corresponding to a vegetable-tanned leather had been reached.

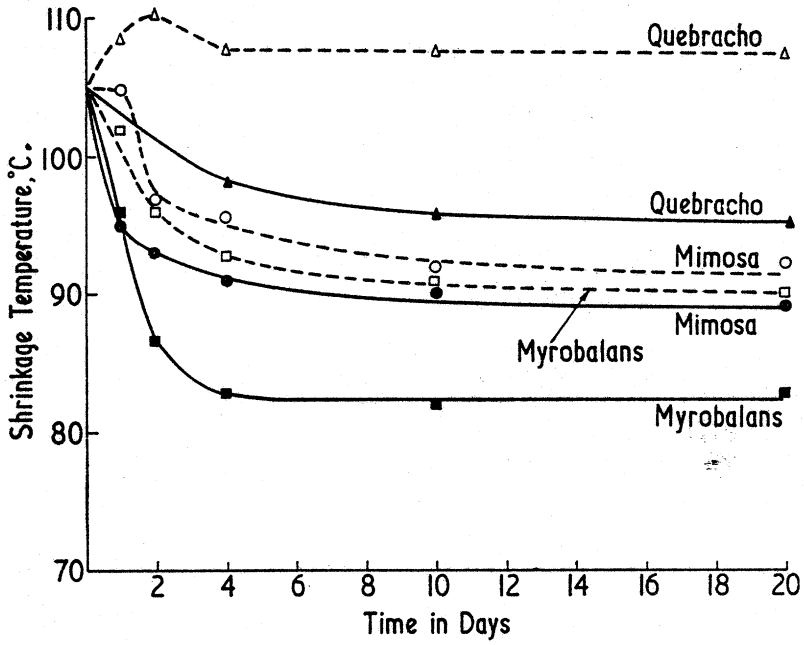

FIGURE 2.—Shrinkage temperature of chrome leather after treatment in tan solutions at 20°C. (broken lines) and 40°C. (continuous lines).

	20°C	40°C
Myrobalans	□	■
Mimosa	○	●
Sulfited Quebracho	△	▲

The possibility existed that the smaller changes in shrinkage temperature occurring with quebracho were related to the rather higher equilibrium pH values found with this material (Table II). The effect of pH was, therefore, examined using this material (Experiment II–Figs. 3 and 4). The initial pH was adjusted to 2.5, 3.0, 3.5, 4.0, and 4.5, and extractions were only made at 40°C. As in the first experiment, the pH fell sharply during the early stages of the extraction, and only minor fluctuations occurred during the subsequent stages. The amounts of chromium extracted increased with time in a similar manner to that observed in the first experiment. Variations of initial pH between 4.5 and 3.5 (final pH values 3.5 to 2.9) had little effect on the chromium extracted, but at the two lowest pH values the amounts extracted were appreciably greater. The shrinkage temperature, however, decreased progressively with pH. As with lactate, these decreases in chromium content and shrinkage temperature can be accounted for by displacement of protein-bound chromium by hydrogen ions (8) and do not necessarily indicate increased complex formation between chromium and the constituents of the vegetable tanning extract. Other evidence, in fact, indicates that such complex formation increases with pH (1).

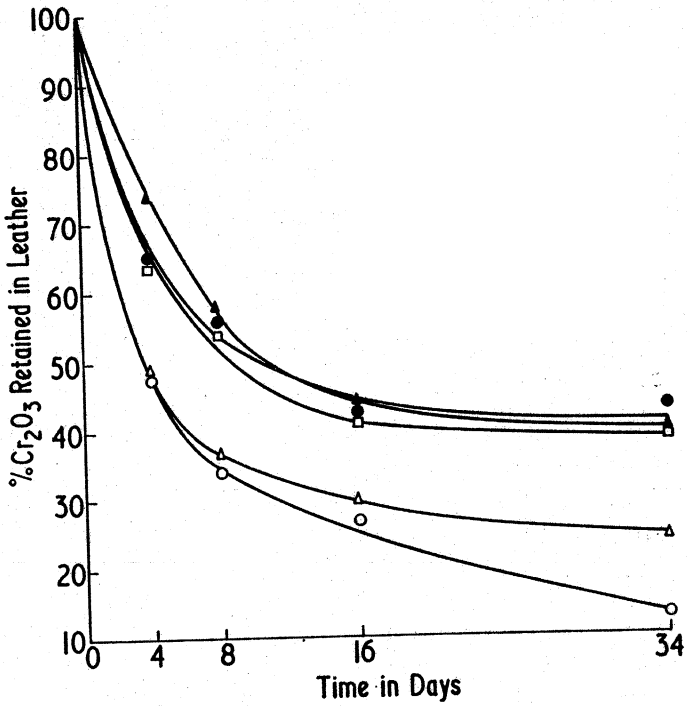

FIGURE 3.—The effect of pH on the percentage chromium retained in chrome leather after treatment in solutions of sulfited quebracho at 40°C.

	Initial pH	Final pH
○	2.5	2.4
△	3.0	2.6
□	3.5	2.9
●	4.0	3.4
▲	4.5	3.5

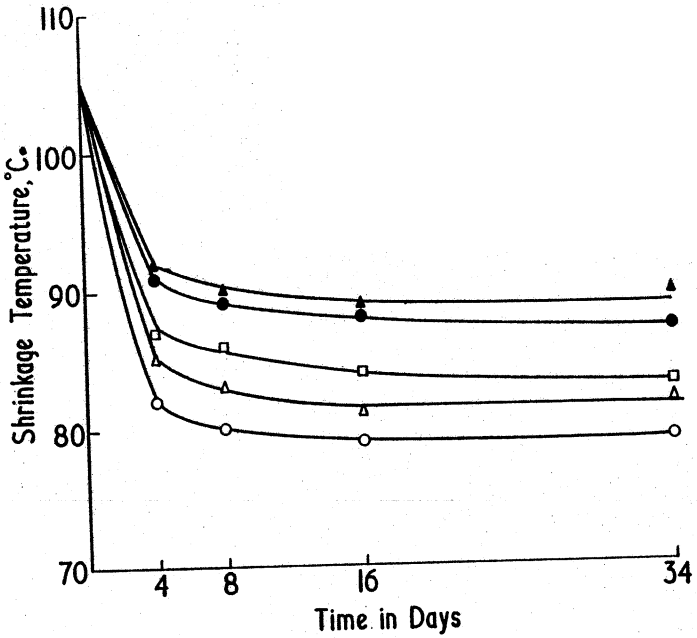

FIGURE 4.—The effect of pH on the shrinkage temperature of chrome leather after treatment in solutions of sulfited quebracho at 40°C.

	Initial pH	Final pH
○	2.5	2.4
△	3.0	2.6
□	3.5	2.9
●	4.0	3.4
▲	4.5	3.5

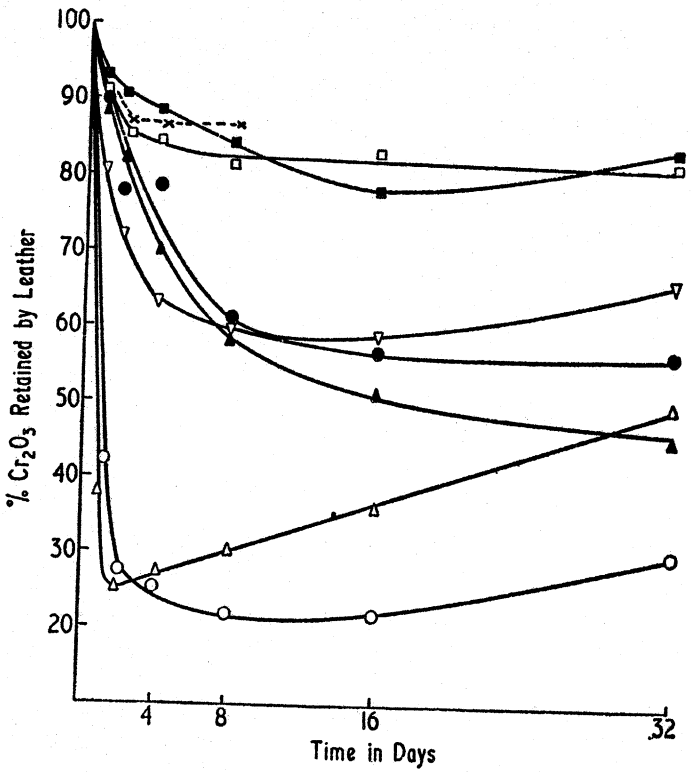

FIGURE 5.—Percentage chromium retained in chrome leather after treatment in solutions of tans and phenolic compounds.

■ Myrobalans
● Mimosa
▲ Sulfited quebracho
▽ Tannic acid
△ Pyrogallol
□ Catechol
○ Resorcinol
× Water

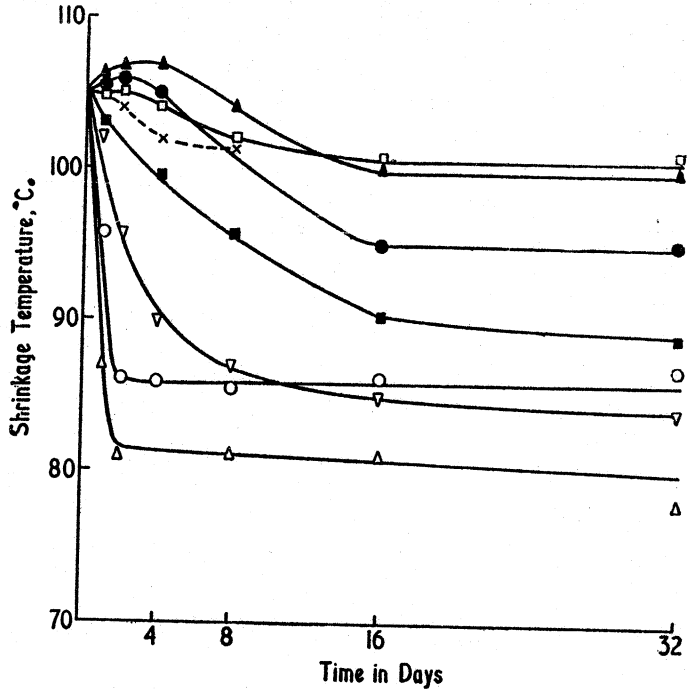

FIGURE 6.—Shrinkage tempreature of chrome leather after treatment in solutions of tans and phenolic compounds.

■ Myrobalans
● Mimosa
▲ Sulfited quebracho
▽ Tannic acid
△ Pyrogallol
○ Catechol
□ Resorcinol
× Water

In the last experiment extractions were made with lower concentrations of tan and extended to 3% solutions of the simpler phenolic compounds, catechol, pyrogallol, and resorcinol. The pH of the extracting solutions was initially adjusted to 4.0

The same general picture was obtained as with the higher concentrations of tan. With myrobalans both losses of chromium and falls in shrinkage temperature were less than with the higher concentrations of tan used in the first experiment; with mimosa and sulfited quebracho, although the falls in shrinkage temperature were less, the amounts of chromium extracted were not noticeably reduced. The initial pH's of the extracting solutions were, however, 0.5 pH units higher than in the first experiment, and precipitation of the tan-chromium complexes may have some bearing on the results (see the next page).

Catechol and pyrogallol extracted over 70% of the chromium in the first two days, but with longer periods of extraction the amounts decreased again. There was no parallel increase in shrinkage temperature, and the higher retention is probably associated with oxidation of the phenolic compounds and precipitation of the chromium complex in the leather. Resorcinol, in contrast to pyrogallol and catechol, extracted little chromium, and the fall in shrinkage temperature was less than 5 °C.

DISCUSSION

All the materials tested, with the possible exception of resorcinol, extracted appreciable amounts of chromium from leather and caused falls in shrinkage temperature of 5 °–25 °C. Extraction of chromium by the vegetable tanning extracts could be due to the nontan organic acid anions which they contain. The rapid displacement of chromium by solutions of pyrogallol and catechol, however, which contain no such anions, lends support to the view that the hydroxyl groups of vegetable tans can also complex with chromium at the expense of protein carboxyl groups. As observed in earlier investigations (1, 7) resorcinol, with hydroxyl groups meta to one another, does not seem to be able to complex in this way.

The extraction of chromium proceeded rapidly during the first few days and then continued more slowly. The shape of the curves, especially when the percentage extraction was plotted on a logarithmic scale, indicates that two processes are involved. These two processes may represent extraction of unipoint and multipoint fixed complexes of chromium or displacement of chromium by organic acid anions and vegetable tan, respectively. The fact that the shrinkage temperature also falls rapidly at first and then more slowly appears to discount the first suggestion, and the rapid extraction by pyrogallol and catechol is against the second. It is possible that the apparently slower extraction in the later stages is associated with the slow fixation by the protein of vegetable tan which has complexed with chromium.

Falls in shrinkage temperature also occurred mainly in the first few days of extraction, but apart from this they did not necessarily run parallel with loss of chromium. For instance, with myrobalans losses of chromium were relatively small, but falls in shrinkage temperature were large; whereas with quebracho losses of chromium approached 50%, while falls in shrinkage temperature were quite small. The amounts of chromium extracted will be dependent on the solubility of the vegetable tan–chromium complex formed. Myrobalans complexes are extensively precipitated at pH values above 2.5, while those formed with quebracho are only precipitated to any appreciable extent when the pH is above 4.0 (1). Variations in the amounts of chromium extracted presumably reflect these differences in solubility. Thus, fall in shrinkage temperature is probably a better guide to the extent of detannage than is the amount of chromium extracted, subject, of course, to the limitation that the shrinkage temperature will approach a value corresponding to vegetable tannage and not continue to decrease with increasing displacement of chromium below this value.

Complex formation between the vegetable tan and chromium and consequent displacement of protein carboxyl groups of the protein is probably the the main factor involved in detannage, but as the pH falls below 4.0, hydrogen ions, by combining with protein carboxyl groups at the expense of chromium, will play an increasing part (8). This effect is illustrated by the results obtained with quebracho, decrease in pH leading to greater falls in shrinkage temperature and, to a lesser extent, increases in chromium extracted. It follows that any fall in pH due to displacement of sulfate ions from the chromium complex or oxidation of the tan (9) will contribute to detannage. The increase in complex formation with increase in pH (1) apparently does not exert much influence on detannage in the range covered.

The three tanning materials tested were compared on an equivalent tan basis, and it may, therefore, be deduced that for a given degree of vegetable retannage quebracho is likely to cause the least stripping of chromium and fall in shrinkage temperature during the actual retannage, and the least detannage and increase in acidity during subsequent storage. Myrobalans is likely to be the worst, and mimosa occupies an intermediate position. Other hydrolyzable tans such as chestnut are likely to behave similarly to myrobalans. Retannage with many syntans can also lead to appreciable losses in chromium (2, 10) and falls in shrinkage temperature (10), and presumably these, too, could cause detannage during storage if present in sufficient quantities.

While small amounts of vegetable tans can apparently protect against the detanning action of lactate ions present in perspiration (10), it will obviously be difficult to strike a satisfactory balance between this protective action and the stripping action involved with larger amounts. The optimum amount

of vegetable tan in relation to chromium will depend on the use to which the leather is to be put and whether perspiration or moist heat is likely to be the primary factor involved in damage.

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